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1. Study on Surface Electricity. (XVII)

Measurement of Interfacial Capacity by Resonance Method Using U-effect

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It was proved in the previous paper that the circuit of U-effect II was equivalent to a combination of the double layer capacity, the solution resistance and the load impedance in series. Hence, we can make a resonance circuit by using an inductive load, which gives maximum current at the value of load reactance satisfying ordinary resonance condition, and estimate the interfacial double layer capacity by resonance measurements.

Experiments were done with an element containing two mercury—N. H_2SO_4 aq. interfaces in series. The resonance curves were obtained with various frequencies and amplitudes of vibration. It was ascertained that capacity values obtained were independent of frequencies as well as of amplitudes of the periodial capacity variation due to the interfacial area changes. We can, therefore, use this method for the capacity measurements at various mercury-solution interfaces.

INTRODUCTION

The studies on the interfacial electrical phenomena were much advanced by the use of a. c. devices, where the factors constituting the equivalent circuits of interfaces are considered to be resistances and capacitances.[1] At mercury-salt solution interfaces within proper regions of polarizing potentials,[2] they are generally called "electrocapillarity",[3] and the capacitances of the interfacial double layers are very important quantities, the parallel resistances (leakages) being almost negligible.[4] From the measurements of the electrical capacitances of such systems we can estimate the values of interfacial tensions, interfacial electrical charge densities, zeta-potentials, etc. and deduce the structures of the interfacial electrical double layers.[3]

In the last section of the preceding paper,[5] we obtained two sorts of application of U-effect II for the interfacial capacity measurement. The former had been used by the present authors under the name of "Impedance Matching Method" and had been reported several times in the foregoing articles,[6] but the latter, which may be called "Resonance Method", had never been put into practice. An attempt was made by the present authors to test its possibility and we shall relate on it here.

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1. PRINCIPLE OF THE METHOD

(1) Resonance Phenomenon

The equivalent circuit of an interface between mercury and salt solution without mercurous ion is very complicated and has not been pictured decisively as yet, but we shall postpone this difficult problem until future articles and assume the most simple model of a combination of a capacitance C and a resistance R_0 in series. This means that the interface is represented by a perfect condenser without leakage and that the solution column is equivalent to a pure resistance. Interfaces of this sort were called by D. C. Grahame[7] "ideal polarized electrodes". As this condenser is supposed to result from orientations of ions and dipoles at interface, it is not a simple *double* layer of positive and negative charges confronting each other, as initially proposed by H. v. Helmholtz,[8] but has a complicated structure consisting of the Stern's adsorption layer[9] and Gouy's diffuse double layer.[10]**

A slight touch was made in the previous paper[5] about the principle of resonance in the case of U-effect II, and we shall make its detailed description here.

The equation representing the current of U-effect II,[5] with inductive and resistive loads in series ($\omega L+R$), is given by

$$\dot{I}=\frac{\dot{V}}{(R_0+R)+j(\omega L-1/\omega K)}, \tag{1}$$

where $\dot{I}$ and $\dot{V}$ are the (complex) amplitudes of the effective values of the alternating current and electromotive force of the circuit, R_0 and K the solution resistance and the average interfacial capacitance and ω the circular frequency, respectively. This equation can be rewritten in the form

$$\dot{I}=\frac{\dot{V}}{\sqrt{R_t^2+(\omega L-1/\omega K)^2}}\,e^{-j\varphi}, \tag{2}$$

where

$$\varphi=\mathrm{tg}^{-1}\frac{\omega L-1/\omega K}{R_t}, \qquad R_t=R_0+R.$$

The modulus of this current (I) reads

$$I=\frac{V}{\sqrt{R_t^2+(\omega L-1/\omega K)^2}}. \tag{3}$$

By changing the value of L continuously, we can get maximum value of I, when the following condition for resonance is satisfied,

$$\omega L=1/\omega K. \tag{4}$$

We put the value of L which fulfils this condition in L_r. The value of the interfacial capacity K is, therefore, calculated from the measurement of L_r. The equation for

this calculation is evidently

$$K = 1/\omega^2 L_r \,. \tag{5}$$

(2) Comparison with Other Methods

For an ideal polarized electrode, the following formula, the so-called "Lippmann-Helmholtz's equation", can be deduced from an exact thermodynamic consideration,[7]

$$(d\sigma/dE)_\mu = q = C_0 E,$$

where σ is the interfacial tension, q the surface electronic charge density of mercury, E the polarizing d. c. potential viz. that of the electrocapillary maximum ($\varphi - \varphi_{max}$) and μ a suffix showing the constancy of the chemical potential (that is, the constancy of composition of the solution phase).

As the interfacial capacity is a function of the polarizing potential, we put the second derivative of the interfacial tension with respect to E in C_0', i. e.

$$(d^2\sigma/dE^2)_\mu = C_0'.$$

From these equations we get the following two capacities,

$$C_0' = d(C_0 E)/dE = dq/dE,$$

and

$$C_0 = \frac{1}{E}\int_0^E C_0' dE = q/E.$$

The former is called the "*differential* capacity" and the latter the "*integral* capacity".

Among the various methods of interfacial capacity measurement, those from the electrocapillary curve[11] and from the impedance bridge[12] give the former values, and that from the increasing mercury surface[11] gives the latter. The method described here gives the differential capacity with an a.c. circuit like the impedance bridge method. As the differential capacity is the more fundamental quantity than the integral capacity, our method is also useful for the structural study on interfacial phases.

2. EXPERIMENTAL DEVICE

(1) Vibrating Element

The vibrating element is a glass capillary containing two mercury-N. H_2SO_4 aq. interfaces in series as is shown in Fig. 1. This is forced to vibrate by a vibrator for

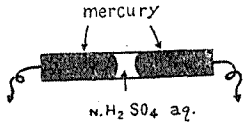

Fig. 1. Vibrating element.

the purpose of a. c. generation by U-effect II. The interfacial capacity per unit area (k μF/cm^2.) is calculated by the equation

$$k = 2K/A,$$

where A is the single interfacial area and K the whole equivalent capacitance calculated from the value of L_r.

(2) Circuit

The measuring circuit is shown schematically in Fig. 2. A vibrator (VIB) forces the element (E) to vibrate with it and to generate an alternating current (U-effect II). The valve oscillator (OSC) is for the purpose of driving the vibrator. The load impedance is the inductometer (L) and the resistance (R) in series. The a.c. current (I) is proportional to the voltage drop at the load resistance (IR), which is measured by a valve-voltmeter (VV) after amplification.

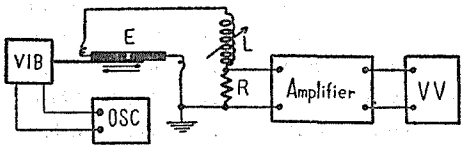

Fig. 2. Block diagram of measuring circuit.

When we change the value of the load inductance (L) continuously, the current of this circuit shows a resonance curve, and we can obtain the resonance point of maximum current ($I=I_r$ at $L=L_r$).

A Brooks-type variable inductometer was used for L, whose inductance varied from 20 to 250 mh. continuously. A non-inductive resistance box was used for R. Amplitudes of vibration were indicated by the readings of the output control of the valve oscillator (GO) in the succeeding tables. These readings are appoximately proportional to the amplitudes of vibration at constant frequency of vibration, but cannot be used for the comparison of them at different frequencies.

3. RESULTS

(1) Resonance Curves

Table 1 gives the readings of the valve-voltmeter for different values of L (from 27.5 to 237.0 mh.) at several frequencies of vibration from 700 to 6,000 cps. They are plotted against L in Fig. 3, which show typical resonance curves at higher frequencies. The curves for lower frequencies do not cover the resonance points in our apparatus. We can detect the resonance points for these frequencies by increasing the range of the inductance value. The slightly humped tendencies observed at lower frequencies were identified by a cathode-ray oscilloscope to be due to the higher har-

Table 1.
Readings of the valve-voltmeter (mA) for several load inductance values at the frequencies named.

L (mh.)	f=700	750	800	900	950	2,000	2,500	3,000	5,000	6,000
27.5	27.5	27.9	33.8	31.1	25.5	116.6	150.5	106.8	103.0	**471.9**
35.2	27.7	28.1	34.0	31.3	25.9	123.5	160.6	117.7	**123.2**	**433.5**
50.3	28.1	28.6	34.7	31.8	26.5	137.2	178.2	147.2	**113.2**	245.0
64.2	28.4	29.1	35.4	32.4	27.1	154.4	254.3	186.6	75.2	144.3
75.9	28.6	29.6	35.9	32.8	27.6	171.5	246.4	229.6	50.1	99.0
86.2	28.9	30.2	36.3	33.3	28.2	188.6	283.7	264.1	36.9	73.6
97.7	29.2	30.9	37.0	33.8	28.8	202.3	326.0	298.5	27.3	55.2
109.5	29.3	31.8	37.8	34.7	29.3	219.5	375.7	**308.8**	19.1	41.7
121.0	29.3	33.0	38.6	35.4	29.5	240.0	424.6	291.3	14.2	34.0
132.2	29.3	34.3	39.5	36.0	29.5	260.6	496.7	255.1	11.0	28.2
143.3	29.9	35.8	40.0	36.5	29.5	281.2	499.4	213.8	8.4	22.9
154.6	30.2	37.4	40.5	36.8	29.4	305.2	**512.6**	175.1	6.7	18.8
166.5	30.2	38.6	40.9	36.6	29.4	331.7	**497.3**	142.1	5.4	16.4
177.9	30.9	39.6	41.0	36.6	29.5	355.0	510.0	116.2	4.3	14.3
188.4	31.2	40.4	41.2	36.4	29.5	377.3	424.6	96.2	3.6	12.7
200.2	31.5	40.9	40.8	36.3	29.5	401.3	374.0	78.4	3.0	11.0
214.7	31.7	41.0	40.2	36.0	29.8	426.0	315.9	62.6	2.5	9.8
229.7	32.5	40.7	39.6	35.8	30.2	440.4	264.0	49.7	2.0	10.0
237.0	32.7	40.3	39.4	35.6	31.2	442.5	244.2	44.8	1.9	8.2
L_r(mh.)							158	109.5	41	28.5
I_r(mA.)							523.6	308.8	130.2	476.5
R(Ω)	400	400	400	400	300	100	100	100	100	100
GO	100	100	100	100	100	20	50	100	20	100

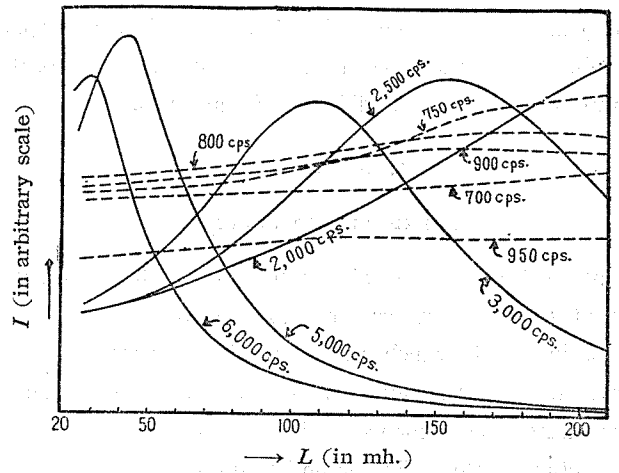

Fig. 3. Resonance curves at frequencies named.
Dotted curves—vertical scale enlarged.

monics of the original vibration.

The interfacial capacity per unit area is calculated from L_r in Table 1 to be about 30 μF/cm^2. (from eq. (5)).

(2) Influence of the Vibrational Frequencies on the Resonance Points

It is obvious from eq. (5) that, for constant value of K, L_r is proportional to $1/\omega^2$. This was demonstrated experimentally by the linearity of the $L_r - 1/\omega^2$ relation in Fig. 4. This plotting is obtained from the data of Table 1.

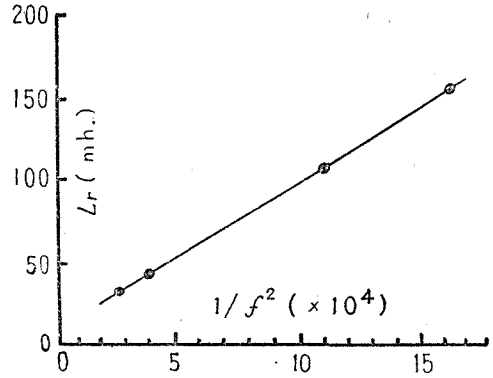

Fig. 4. Plots of L_r *versus* $1/f^2$, showing linear dependence.

(3) The Influence of the Vibrational Amplitude on the Resonance Points

As was shown in the preceding article,[5] the equivalent capacitance c of interface is not constant, but changes periodically in our case, i.e.

$$c = K + \Delta c,$$

and

$$\Delta c = \sqrt{2}\,\Delta C e^{j\omega t}.$$

To examine the influence of this change of the interfacial capacitance on the resonance point, we measured the resonance curves for various values of the oscillator output (GO) at constant frequency of vibration (at 2,500 cps.). The results are shown in Table 2, which shows that the values of L_r do not depend on the amplitudes of capacitance change within the region used in our experiments.

This result is interpreted by the fact that the resonance curves are the plottings of the readings of the valve-voltmeter, which show the time *averages* of the current of the circuit. It must be noted, however, that the Q-values are *not* so, as will be shown in the next article.

Table 2.
Readings of the valve-voltmeter (mA) for several load inductance values at vibration amplitudes named (GO).
f=2,500 cps., R=500Ω.

L (mh.)	GO=100	20	10	5	3
27.5	52.3	29.4	11.9	1.4	0.3
35.2	56.0	32.0	13.1	1.6	0.4
50.3	62.4	37.4	15.8	2.3	0.6
64.2	69.6	42.6	18.6	3.1	0.8
75.9	75.7	46.5	21.2	4.0	1.1
86.2	81.8	51.5	23.7	4.8	1.3
97.7	88.5	55.5	26.6	5.6	1.6
109.5	94.6	61.4	29.6	6.6	1.9
121.0	99.7	65.1	31.9	7.5	2.2
132.2	103.0	67.1	33.5	8.3	2.4
143.3	104.2	68.0	33.6	8.5	2.5
154.6	103.1	68.0	33.3	8.3	2.4
166.5	99.6	63.0	31.4	7.8	2.2
177.9	94.6	61.0	29.2	6.9	2.1
188.4	89.0	55.3	26.6	5.9	1.7
200.2	82.3	51.0	23.6	5.0	1.4
214.7	74.0	44.8	20.2	4.0	1.2
229.7	65.6	38.5	17.0	3.2	1.0
237.0	62.3	36.5	15.5	2.9	0.9
L_r(mh.)	142	142	142	142	142

CONCLUSION

We have so far described one of the applications of U-effect II for the measurements of interfacial double layer capacities, and it has been proved experimentally that this effect is also applicable for this measurement as well as the impedance matching method.

While the impedance matching method requires two independent measurements of current and voltage, the one described here requires only one measurement (of current), which is the superiority of this method in its simplicity of operation. In addition, the easiness in obtaining the maximum point of current makes it a better one for the capacity measurement compared with many others.

The authors wish to express their gratitude to Prof. I. Tachi for his continued interest and encouragement.

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** According to D.C.Grahame,[7] the leakage current is as small as $10^{-3}\sim10^{-4}$ Amp./cm^2. the interface of mercury and the solution without mercurous ions within a certain region of potential (outside which there occur electrolytic reactions). The frequency effect of the conductivity in solution as discovered by Falkenhagen is of course quite negligible within the frequency range used in our experiments.